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Research Report

**Fabrication of high-performance polymer bulk-heterojunction
solar cells by the interfacial modifications II.**

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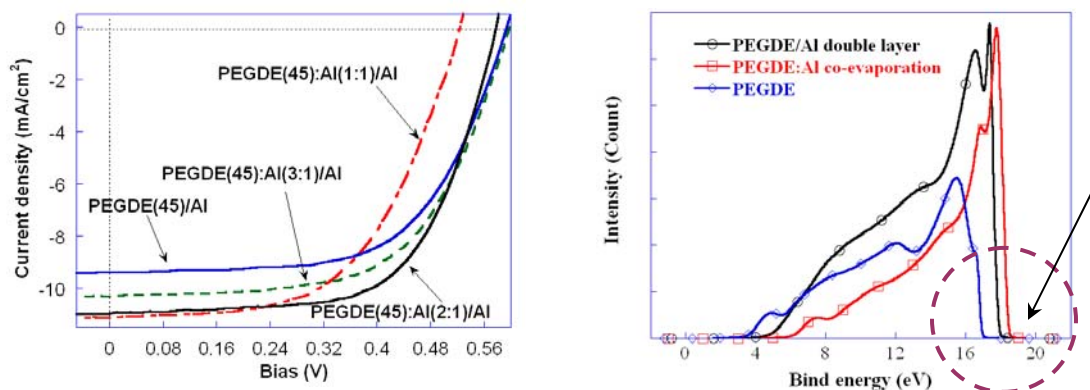
I. Abstract

This research investigates three primary tasks for fabrication of high performance polymer-bulk-heterojunction solar cells. i) The development of the very unique poly(ethylene-oxide) functionalized polymer:Al complex electrode through an co-evaporation process for polymer BHJ solar cells. ii) Modification of TiO₂/ITO by self-assemble monolayer for inverted-type polymer electronic devices iii) The studies of magneto responses for P3HT and P3HT:PCBM photovoltaic cells made of intrinsically non-magnetic organic components.

II. Progress summaries

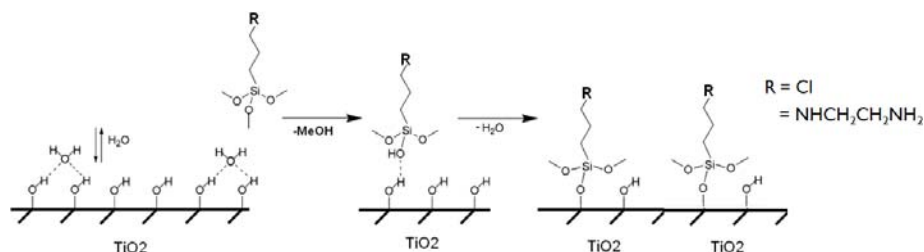
(i) The development of the very unique poly(ethylene-oxide) functionalized polymer:Al complex electrode through an co-evaporation process for polymer BHJ solar cells

The P3HT:PCBM-based BHJ solar cells were prepared by co-evaporating the poly(ethylene-oxide) functionalized polymer with Al metal as complex electrodes at different deposition ratio in vacuum. The result of this experiment confirmed the instant organic:metal reaction during the deposition of electrode, in which the metal complex was characterized by the XPS and UPS analysis at National Synchrotron Radiation Research Center, Taiwan and essentially important to the enhanced performance of P3HT:PCBM solar cells. The *I-V* curves of P3HT:PCBM-based polymer BHJ solar cells with configurations of ITO glass/PEDOT:PSS/P3HT:PCBM/PEGDE:Al(1:1, 2:1, and 3:1, 5 nm)/Al(100nm) and ITO glass/PEDOT:PSS/P3HT:PCBM/PEGDE(4.5 nm)/Al(100nm) under 1.5G illumination are presented in the following figure. The device of PEGDE(4.5 nm)/Al double-layer electrode device has the *PCE* of ~3.4%. The device performance is modulated by the PEGDE:Al co-evaporation ratio of the electrode, which has a maximum *PCE* of ~4.0%, *FF* of 0.63, while the PEGDE:Al(2:1, 5 nm)/Al was used as the complex electrode. The UPS measurement, shown in the following figure, confirmed the result that the work function of organic oxide/Al electrode is changed with the co-evaporation process. The result also suggests the PEGDE:Al co-evaporation electrode is more favorable for the fabrication of P3HT:PCBM-based solar cells.



(ii) Modification of TiO₂/ITO by self-assemble monolayer for inverted-type polymer electronic devices

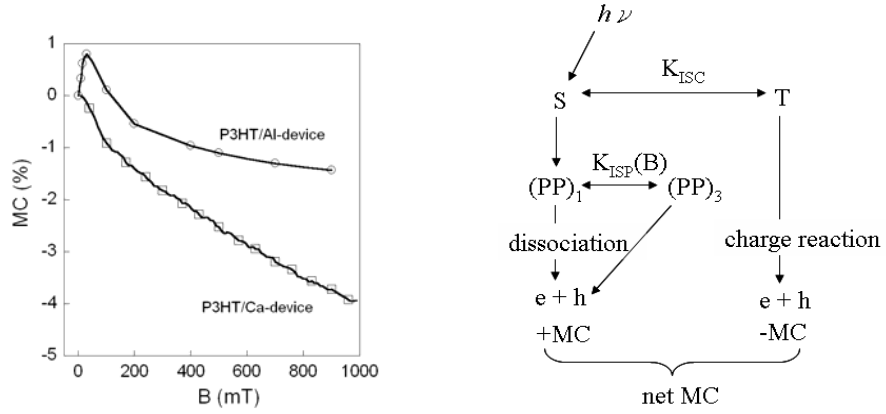
Two silane-based self-assemble monolayer with different terminal groups had been applied to modify the TiO₂/ITO substrate to facilitate the transport of charge carriers. The mechanism of silanization is shown in the following figure. The presence of an amine group at the outer surface of N-[3-(trimethoxysilyl)propyl]ethylenediamine (PEDA-TMS)-modified substrate induces a strong dipole due to its low electronegativity, which lowers the work function of the cathode. Our current result indicated that the inverted light-emitting diodes of modified TiO₂/ITO substrate have the higher efficiency and better environmental stability. The test of the modified TiO₂/ITO substrate for polymer solar cells is still in progress.



(ii) The studies of magneto responses for P3HT and P3HT:PCBM photovoltaic cells

The mechanisms to interpret the magneto conductance (MC) responses for polymer photovoltaic devices made of P3HT and P3HT:PCBM as the active layers are presumably correlated with the influence of the applied magnetic field and electrical bias on the photo- and electrical-excited states (excitons and PP states) and intermolecular charge-transfer complexes of conjugated molecules. Our results have indicated that the MC responses can be modulated to yield positive, negative, and/or inverse effects by the photo illumination, the usage of different metal electrodes, interfacial dipole layer, the applied magnetic field and electrical bias, and the composition of polymer active layers. The polymer photovoltaic cells made of the same P3HT layers, P3HT/Al- and P3HT/Ca-device have the distinct MC response as shown in the following figure. The

mechanisms for the MC responses of polymer photovoltaic cells is also proposed in the following figure. As for P3HT:PCBM-based bulk-heterojunction photovoltaic cells, the charge-transfer complexes would be the critical excited states to influence the overall power conversion efficiency.



III. Summary of Accomplishments

1. "The magneto conductance responses in polymer photovoltaic devices" *Org. Electron.* **11**, 677 (2010). (AOARD-09-4055) (Joint research work with Prof. Bin Hu at University of Tennessee)
2. "Nano-scale mechanical properties of polymer/fullerene bulk hetero-junction films and their influence on photovoltaic cells" Submitted to *Carbon* and currently under the review (2010). (AOARD-09-4055)
3. "Magnetoeconductance responses in conjugated molecules of charged polaron pairs" in preparation (2010). (AOARD-09-4055) (Joint research work with Prof. Bin Hu at University of Tennessee)
4. "Magnetovoltaic effect in polymer charge-transfer complex diodes" in preparation (2010). (AOARD-09-4055) (Joint research work with Prof. Bin Hu at University of Tennessee)
5. "The polymer gate dielectrics and source-drain electrodes on n-type pentacene-based organic field-effect transistors" *Org. Electron.* **11**, 1613 (2010). (AOARD-09-4055)
6. "Selective manipulation of microparticles using polymer-based optically induced dielectrophoretic devices" *Appl. Phys. Lett.* **96**, 113302 (2010). (AOARD-09-4055)

7. "Bulk-heterojunction polymers in optically-induced dielectrophoretic devices for the manipulation of microparticles" *Optics Express* **17**, 17603 (2009). (AOARD-09-4055)
8. "Surface modification of TiO₂ by a self-assembly monolayer in inverted-type polymer light-emitting devices" *Org. Electron.* **10**, 1626 (2009). (AOARD-09-4055)
9. "White-emissive tandem-type hybrid organic/polymer diodes with (0.33, 0.33) chromaticity coordinates" *Optics Express* **17**, 21205 (2009). (AOARD-09-4055)

IV. The magneto conductance responses in polymer photovoltaic devices

Abstract

This work studies the magneto conductance (MC) responses of regioregular poly(3-hexylthiophene) (P3HT)-based polymer photovoltaic devices. The net MC results of devices are the sum of the positive and negative MC effects. The positive MC effect is due to the increased population of the singlet polaron-pair (PP) states (of the high dissociation rate to charge carriers) under the magnetic field. The negative MC effect results from the decline on the triplet exciton-charge reactions to charge carriers (the mobility and concentration of triplet excitons are decreased by the magnetic field). The MC responses of P3HT-based photovoltaic devices can be manipulated by the applied magnetic field, the electrical bias, the built-in potential, and the interfacial dipole layer. An inversion in the MC response is observed at the electrical bias near the open-circuit voltage. In addition, blending of an electron acceptor material, [6,6]-phenyl C61-butyric acid methyl ester, in P3HT active layer quenches the photo-excited states at the donor-acceptor interface and results in distinct MC responses of photovoltaic cells, which probably are related to the features indicating the formation of intermolecular charge-transfer complexes at donor-acceptor junction.

Keywords; bulk-heterojunction, solar cell, photovoltaic cell, magneto conductance, polaron-pair

1. Introduction

Organic conjugated molecules/polymers have very unique properties, [1-3] they can be used as organic semiconductors in fabricating novel electronic devices. [4-9] In addition, the electronic devices incorporating organic conjugated molecules/polymers as the active layers, exhibit strong magneto responses. [10, 11] The output performance, such as the electroluminescence, [10, 12-14] resistance or conductance, [10-16] and photocurrent [11, 17-20] in organic/polymer diodes and photovoltaic (PV) cells can be modulated by the applied magnetic field, although the basic device configurations are composed of intrinsically non-magnetic components. The magneto responses of organic semiconductors would have new applications in organic electronics and spintronic devices. [21-24]

A large magneto resistance (MR) or magneto conductance (MC) response in organic/polymer light-emitting diodes (O/PLEDs) has been reported by many researchers, which is intimately associated with the threshold of light emission and the ambipolar injection of charge carriers. [10, 25] While the organic/polymer diodes are operated at PV regime with illumination, the magnitude of photocurrent is varied with the applied magnetic field. [11, 17-20] These results suggest that the dissociations and charge-reaction processes of the photo-excited states to the generation of free charge carriers are susceptible to changes by the applied magnetic field. The excited states, induced either electrically (in O/PLEDs) or optically (in PV cells) in organic semiconductor layers, are essentially important to the MR or MC responses in organic/polymer diodes and PV cells. [26-30]

The excited states (excitons) in the regioregular poly(3-hexylthiophene) (P3HT)-based polymer diodes are coulombically bound electron-hole (e-h) pairs, commonly having a short range of the separation distance. [27, 31-34] Those excitons may undergo a relaxation process to become the excited polaron-pairs (PP) states with a longer range of e-h separation distance than that of excitons. Figure 1(a) illustrates the schemes for formation of intra- and inter-molecular excited PP states from excitons. Both the excitons and PP states are the excited states of conjugated organic molecules possessing singlet and triplet electronic configurations. The lifetime of the singlet and triplet PP states is shorter than that of the singlet and triplet exciton states. [35, 36] The magnitude of exchange energy for the singlet/triplet excited states is exponentially decayed with respect to the e-h separation distance and is related to the energy difference between singlet and triplet states. [31, 32] Accordingly, the status of the long-range (>1 nm) PP states having exchange energies of the order smaller than 10^{-3} meV is subjected to changes brought in by the applied magnetic field. Sakaguchi *et al.* reported that the

external magnetic field dependencies on the photodecomposition reaction in solution, which were attributed to the electronic Zeeman and hyperfine interactions in the intermediate radical pair. [37] The intersystem crossing process of singlet/triplet PP states as illustrated in Fig. 1(b) involves the spin orbital coupling (SOC) [38, 39] and the hyperfine interaction (HFI). [19, 27, 40-43] The population of singlet and triplet PP states can be modified by the external magnetic field, such as the changes of the splitting and difference of the energy states by Zeeman effect. [19, 27, 29] Since the photocurrent of P3HT-based diodes is the sum of “current flows” generated by the photo-excited states (excitons and PP states), any variations induced by an applied magnetic field on the distribution, dissociation, and charge reaction processes of the singlet/triplet excited states (excitons and PP states) would certainly modulate the magnitude of photocurrent and MC response in PV devices. [18, 30] In this manuscript, we studied how the change of the electrical bias and the device electrode influences the dissociation and charge reaction processes of photo-excited states in P3HT-based polymer diodes. Increasing the applied magnetic field increases the distribution of singlet PP states and reduces the mobility of triplet excitons by Zeeman splitting. [29, 30] The dissociation rate of the singlet PP states is higher due to the stronger ionic feature than that of triplet PP states, [19, 44, 45] which is accountable for an increase of free charge carriers and a positive MC effect. However, the decline of triplet excitation-charge reactions to charge carriers (reduce in mobility and concentration of triplet excitons), caused by the applied magnetic field, [46-48] results in the decrease of free charge carriers and contributes to a negative MC effect. The net MC responses of the photovoltaic cells are the sum of positive and negative MC effects, in which the processes are schematically illustrated in Fig. 1 (c). Additionally, the MC responses are influenced by built-in electrical field of the diodes, which is tunable by varying the bias voltages and the work function of electrodes. An inversion in MC response is observed at the electrical bias near the open-circuit voltage (V_{oc}). The magneto responses for intermolecular charge-transfer complex states at the donor-acceptor interface are investigated by blending an electron acceptor material, [6,6]-phenyl C61-butyric acid methyl ester (PCBM), in P3HT as the active layer. The distinct MC features suggest the formation of intermolecular charge-transfer complexes at donor-acceptor junction.

2. Experimental Section

The polymer diodes and photovoltaic devices are fabricated in a standard arrangement by sandwiching the active layer between a transparent electrode and a metal

electrode. The transparent electrode is comprised of the cleaned indium-tin-oxide (ITO) covered glass substrate (RITEK Corp., $15 \Omega/\square$) coated with poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS; Baytron P, Bayer AG, Germany) layer. Regioregular organic P3HT (98.5% electronic grade, Rieke Metals, Inc., USA) and PCBM (procured from Nano-C, USA) are dissolved in dichlorobenzene to yield the P3HT (20 mg/ml) and P3HT:PCBM (20:20 mg/ml) solutions. The active layers are obtained by spin-coating the solutions on the PEDOT:PSS/ITO/glass substrates at the drying process of the films in a slow-growth regime. [49, 50] The thicknesses of P3HT and P3HT:PCBM films are approximately $160 \text{ nm} \pm 10 \text{ nm}$ and $200 \text{ nm} \pm 10 \text{ nm}$, respectively. [51] Ca (40 nm) and Al (100 nm), as metal electrodes, are thermally deposited onto the surface of the active layer inside a vacuum chamber ($4.0 \times 10^{-6} \text{ hPa}$).

A halogen lamp is used as the light source (80 mW/cm^2) to investigate the MC response of the photovoltaic cells in this study. The devices are encapsulated by the UV-curable epoxy with a cover glass and placed at the direction parallel to the magnetic field. In order to eliminate the influence due to drifting with different bias voltages, the MC curves are averaged, based on the approach reported by Desai *et al.* [13]. The MC magnitude presented in this manuscript is defined as;

$$MC = \frac{\Delta I(B)}{I(0)} = \frac{I(B) - I(0)}{I(0)} \quad (1)$$

Where $I(B)$ and $I(0)$ are the current intensity of the photovoltaic cells with and without the applied magnetic field, respectively. All the measurements are performed at room temperature. The magneto conductance of polymer diodes in our study is found to be independent of external magnetic field's direction. [20] The schematic drawings of the device configuration, the measurement of MC responses for polymer diodes under the applied magnetic field with illumination, and the chemical structures of P3HT and PCBM in this study are illustrated in Figure 2(a). Figure 2(b) presents the emission spectrum of halogen lamp and the absorption spectra of P3HT and P3HT:PCBM films used in this studies. The spectrum overlap are high for the emission of the halogen lamp and absorbance of P3HT and P3HT:PCBM films.

3. Results and discussion

3.1 Effect of applied magnetic field and device electrodes on MC responses

Figure 3 presents the measured MC of the short-circuit current (I_{sc} , photocurrent measured at 0V bias voltage) for devices with the configurations of ITO/PEDOT:PSS/P3HT/Al (P3HT/Al-device) and ITO/PEDOT:PSS/P3HT/Ca/Al

(P3HT/Ca-device) with illumination. MC response of the I_{sc} for P3HT/Al-device is positive and sharply increased from 0% to 0.8% in the low magnetic field (<30 mT) and then gradually decreased as the applied magnetic field is increased. The MC of P3HT/Al-device is reduced to zero and inversed from positive to negative at the applied magnetic field near $B \sim 150$ mT, and is of $\sim -1.4\%$ at $B = 900$ mT. The positive and negative MC response of the I_{sc} for P3HT/Al-device is modulated by the applied magnetic field.

As illustrated in Fig. 1 (c), the singlet excitons (S) can dissociate into inter-molecular singlet PP states ((PP)₁) due to their lower binding energies towards the generation of photocurrent as compared to that of triplet excitons (T). The singlet PP states ((PP)₁) can partially convert into triplet PP states ((PP)₃) through the intersystem crossing process. Excitons and PP states in singlet and triplet configurations can be involved in the dissociation and charge-reaction processes to generate the photocurrent. In PP states, an external magnetic field can cause an external Zeeman splitting on triplet states and thus change the intersystem crossing if the external Zeeman splitting is greater than the internal Zeeman splitting. This suggests that an external magnetic field can increase the singlet/triplet population ratio in inter-molecular excited states (PP states). [52]

Kalinowski *et al.* reported the dissociation rates are different for singlet and triplet PP states ($k_1 \gg k_3$) due to the fact that singlet PP state has a stronger ionic character than triplets and therefore singlet PP states are stronger coupled with the ionic reaction products of separated holes and electrons. [19] Tandon *et al.* suggested both the original pair of polarons and the singlet exciton state are ionic in nature, whereas the triplet exciton is covalent. [45, 53] Accordingly, the singlet PP states have higher dissociation rate than that of triplet PP states is reasonably assumed in our work.

Xu *et al.* also suggested that a low magnetic field (<30 mT) usually affects the formation rate of singlet/triplet PP states at the relaxation process of photo-excited excitons. [18, 30] The increased distribution of singlet PP states by the applied magnetic field raises the I_{sc} (singlet PP states have a relatively higher dissociation rate for converting into free charge carriers than that of triplet PP states), [27, 19] and contributes to a positive and sharply elevated MC response in the low magnetic field for P3HT/Al-device.

Although the initial excited states in P3HT by photo illumination are singlet based on the selection rule, the singlet excited states can be partially converted into triplet excited state through intersystem crossing caused by internal magnetic interaction from SOC and HFI. Both singlet and triplet excitons can exist in P3HT active layer under the illumination. The densities of triplet exciton of P3HT under illumination are about 77%

as reported by Burrows *et al.* [54] for the study of S1~>T1 intersystem crossing in pi-conjugated organic polymers. It is noticed that there's no heavy atoms in the system.

As the applied magnetic field is gradually increased, the decrease of triplet exciton-charge reactions causes a simultaneous reduction in the I_{sc} and accounts for a negative MC response. The exciton-charge reaction is essentially Coulombic interaction between an excited state and a trapped or free charge carrier. [55, 56] The studies of phosphorescence and delayed fluorescence quenching effect indicate that the excitons can interact with trapped charge carriers to de-trap the charge carriers. [46, 57, 58] Alternatively, the triplet excitons can react with free charge carriers in organic materials to dissociate the electron-hole pairs. [47, 59] However, a magnetic field can decrease the reaction-rate constant by removing the triplet degeneracy or deducing the triplet mobility due to the external Zeeman splitting. [26, 29, 40, 57] The triplet exciton charge-reactions can be decreased with magnetic field and yield a negative component in MC effect. Although the exciton-charge reactions of both singlet and triplet excitons can contribute the device current, the influence of the applied magnetic field on the exciton-charge reaction of the triplet excitons is more apparent, probably due to their longer diffusion length and sufficient contacts with charge carriers than those singlet excitons. It is assumed that the change on the exciton-charge reaction of the singlet excitons by the magnetic field is not comparable to that of the triplet excitons. The triplet exciton-charge reactions are decreased with magnetic field and yield a negative component in MC effect. The other possibility of the negative MC effect on I_{sc} is a reduction in the initial concentration of triplet excited states. An external magnetic field can increase singlet/triple population ratio in inter-molecular excited states (PP states) by reducing the intersystem crossing within PP states, [52] that would lead to a decrease in the population of triplet PP states and consequently in the concentration of triplet excitons. As a result, the current due to the exciton-charge reaction of triplet excitons should be decreased and contributed to the negative MC effect on I_{sc} . The magnetic-field dependence of the I_{sc} for P3HT/Al-device can be attributed to the tradeoff between the distribution and dissociation of the singlet PP states (positive MC response) with the changes on the triplet exciton-charge reactions to charge carriers (negative MC response) under the influence of applied magnetic field.

While the Ca is used instead of Al as the metal electrode for P3HT-based polymer diode, the MC curve of P3HT/Ca-device is negatively increased with the applied magnetic field (unlike that of P3HT/Al-device), as show in Fig. 3. Since the interfacial barrier height at the polymer/metal junction is reduced by the low work function Ca electrode, P3HT/Ca-device has a better polymer/metal interface for the generation and

collection of charge carriers than that of P3HT/Al-device, as applied for photovoltaic cells [60, 61]. Alternatively, the high built-in potential of P3HT/Ca-device would accelerate the dissociation of the polaron-pair states in P3HT layer without the magnetic field that would improve the charge extraction. (The magnitudes of V_{oc} are $\sim 0.25\text{V}$ and $\sim 1.01\text{V}$ for P3HT/Al-device and P3HT/Ca-device, respectively.) Noted that MC effect is defined by the current ratio with and without the magnetic field. The improvement of the charge extraction without the magnetic field did not contribute the MC response. Since most of the polaron-pair states probably are dissociated due to the higher built-in electrical field in P3HT/Ca-device, the exciton-charge reactions of triplet excitons would be the dominated mechanism. The charge reaction of triplet excitons are reduced as the applied magnetic field is increased, which decreases the overall photocurrent and hence results in net negative MC responses. The MC of P3HT/Ca-device is of $\sim -4.0\%$ in an applied magnetic field of $B=1000\text{mT}$.

The devices with the configuration of ITO/PEDOT:PSS/P3HT/LiF/Ca/Al (P3HT/LiF/Ca-device) are also fabricated to investigate the influence of the additional dipole layer at P3HT/Ca interface on MC responses. Figure 4 illustrates the MC curves of the I_{sc} for P3HT/LiF(X nm)/Ca-device with varied thicknesses of LiF layers. The measured MC responses of I_{sc} in an applied magnetic field of $B=1000\text{mT}$ are of $\sim -4.0\%$, -2.9% , and -2.3% for P3HT/LiF(X nm)/Ca-device of $X=0, 1.5$, and 5.0 nm , respectively. The magnitudes of MC responses decrease with increasing thickness of LiF layer. These results suggest that the additional dipole layer (LiF) functions as an electrical dipole field to accelerate the dissociation of the photo-excited states near (or diffused to) the polymer/metal junction, but lower the influence of the applied magnetic field on the triplet excitons. The inset of Fig. 4 presents the thickness of LiF layer versus MC response at $B=1000\text{mT}$ and I_{sc} plots. The magnitudes of I_{sc} are increased with the thickness of interfacial dipole layer, which are of $0.007, 0.023$, and 0.076 mA/cm^2 for P3HT/LiF(X nm)/Ca-device of $X=0, 1.5$, and 5.0 nm , respectively, and are associated with the decreased magnitude of MC responses. The interaction of the photo-excited states with electrodes is important to determine of the magnitude of I_{sc} and MC responses of P3HT-devices in our studies. Recent publications by Kalinowski *et al.* and Lei *et al.* had reported the photocurrent and device current are partially contributed by the exciton-induced injection of electrons.[62, 63] MC responses of tri(8-hydroxyquinoline) aluminum (Alq3)-based diodes are possibly due to the magnetic field modulation of the stream of singlet excitons reaching the cathode as proposed by Kalinowski *et al.*.[52]

3.2 The effect of electrical bias on MC responses

Figure 5(a) presents the MC curves of P3HT/Ca-device with illumination at various bias voltages. The MC responses are of $\sim -4.0\%$ for the P3HT/Ca-device biased at 0.00 V and 0.50 V in an applied magnetic field of $B=1000$ mT, and they significantly increase to $\sim -6.2\%$ and $\sim -23.0\%$ when the devices are biased at 0.90V and 1.00V, respectively. However, the MC response is reversed from negative ($\sim -23.0\%$ at 1.00V) to positive ($\sim 2.0\%$ at 1.10V) as the bias voltage was raised to 1.10V and is almost vanished ($<0.1\%$) at a bias voltage that exceeds 1.50 V. Figure 5(b) plots the MC curve of the P3HT/Ca-device with illumination versus bias voltage and semi-logarithm current-voltage (J - V) plot at $B=1000$ mT. The inversion of the MC curve is found at the bias voltage close to the V_{oc} in the semi-logarithm J - V plot.

The photo-excited states in P3HT active layer are the Coulombically bound e-h pairs. The Coulombic interaction of those excited e-h pairs is varied with the separation distance and is subjected to change with magnitude and direction of the internal (built-in electrical field: difference in the work function of two electrodes) and external (the applied bias) electrical fields. As the applied bias voltage of P3HT/Ca-device approaches V_{oc} , the influence of the built-in electrical field on the Coulombically bound e-h pairs is minimized, because the built-in electrical field is offset by the applied electrical bias ($V-V_{oc} \sim 0$). The internal and external electrical fields are of opposite directions at the bias regime in which the applied voltage is lower than the V_{oc} . As a result, the denominator $I(0)$ in Eq. (1) is nearly zero as the bias voltage approaches V_{oc} . Therefore, a drastic MC response (negative) as calculated by Eq. (1) at an applied bias voltage close to V_{oc} is observed as shown in Fig. 5(a) and (b). However, the influence of the applied magnetic field on the I_{sc} at the electrical bias approaches V_{oc} should also be considered as a factor for the significant increase of MC responses. Noted that it requires the very delicate control to precisely measure the current (very small magnitude) at the effective electrical field of the device down to zero ($V-V_{oc} \sim 0$). The $I(0)$ and $I(B)$ for P3HT/Ca-device biased at the voltages, 0.90V and 1.00V (very close, but not equal to V_{oc}), are of -8.51×10^{-4} mA/cm² and -7.98×10^{-4} mA/cm², 9.28×10^{-4} mA/cm² and 7.15×10^{-4} mA/cm², respectively. Although the device current at the bias voltage very close to the V_{oc} is small, the finite differences, $I(B)-I(0)$, of -0.53×10^{-4} mA/cm² and -2.13×10^{-4} mA/cm² correspond to the -6.2% and -23.0% of MC responses for the device biased at 0.90V and 1.00V, respectively. These results probably suggest that the MC responses at the bias voltage close to V_{oc} (the effective voltage $V-V_{oc} \sim 0$) would be determined by the influence of the applied magnetic field on the photo-excited states, in which the mechanism for the

decrease in exciton-charge reactions of the triplet excitons are eminent as mentioned in the previous paragraph and thus results in the maximum (negative) MC responses.

The injection of charge carriers occurs at the bias voltage larger than V_{oc} . Firstly, $I(0)$ is exponentially increased in this bias regime. Secondly, the excited states in P3HT active layer should include the electrical-induced excitons and PP states from the recombination of the injected and oppositely-charged carriers. Thirdly, the Coulombic interactions of those excited (photo- and electrical-induced) states may be reduced (or the average intercarrier distance of excited states is changed) by the external electrical field at the bias voltage larger than the V_{oc} , which affects strongly the energy gap between the singlet and triplet excited state and influences the mixing of the spin states. The increased distribution of singlet PP states under the influences of the magnetic field at the bias voltage larger than the V_{oc} probably contributes a positive MC response. The MC curve is positively increased and inversed from $\sim -23.0\%$ at 1.00V to $\sim 2.0\%$ at 1.10V when $B=1000\text{mT}$. However, the MC response is almost suppressed as the current densities or bias voltages increase. This result can be interpreted by the current generated due to the formation and dissociation of excited states under the influence of external magnetic field only and accounts for a relatively small amount of the total current density. The denominator $I(0)$ is exponentially increased at the bias voltage larger than V_{oc} , which is responsible for a relatively small MC response based on the calculation in the Eq. (1). The above summaries fortify the assumption that the measured MC is basically associated with the interaction of excited states with the applied magnetic field and electrical bias.

3.3 Features of intermolecular charge-transfer complexes on MC responses

Figure 6 illustrates the MC curves of P3HT/Ca-device and P3HT:PCBM/Ca-device at the applied bias voltage, 2.00V and 0.70V, respectively, larger than its V_{oc} without illumination. For the P3HT/Ca-device, a positively increased MC response is observed at the low magnetic field ($B < \sim 200\text{ mT}$), which is associated with the dissociation of electrical-excited PP states from the injected charge carriers (without illumination and the bias voltage large than V_{oc}) as facilitated by the applied electrical and magnetic field. However, the influence from the applied electrical and magnetic field on the total current density of P3HT/Ca-device reaches a saturated level at $B > \sim 400\text{ mT}$. Further increasing the applied magnetic field above $\sim 400\text{ mT}$ did not enlarge the MC response and account for a flat MC curve as shown in Fig. 6.

Blending an electron acceptor, (PCBM), with P3HT as the active layer (a

bulk-heterojunction conjugated system) effectively causes the charge separation of the excited states at the donor-acceptor (P3HT-PCBM) interface and therefore markedly changes the MC responses as illustrated in Fig. 6. The MC curve of P3HT:PCBM/Ca-device without illumination is almost inhibited (showing a flat line close to zero) at the low magnetic field from 0 to ~180 mT, but is positively increased with the applied magnetic field at $B > \sim 180$ mT. The observation of MC curves for the P3HT:PCBM/Ca-device in Fig. 6 confirms very well the characteristic features for the existence of the intermolecular charge-transfer complexes at the donor-acceptor interface. [30] The dissociation of the intermolecular charge-transfer complexes is interrupted by the strong Coulmbic interactions in donor-acceptor molecules at the low magnetic field. Therefore, the MC curve is almost zero and has a threshold of increase at $B \sim 180$ mT. The increased distribution of singlet intermolecular charge-transfer complexes states due to the magnetic-field-dependent intersystem crossing by the applied magnetic field ($B > 180$ mT) raises the I_{sc} through the dissociation of singlet charge-transfer complex, which are responsible for the positively increased MC response of P3HT:PCBM/Ca-device.

Figure 7(a) presents the MC curves of P3HT:PCBM/Ca-device with illumination at various bias conditions. Figure 7(b) plots the MC curve of the P3HT:PCBM/Ca-device with illumination versus bias voltage and semi-logarithm J - V plot at $B = 1000$ mT. The MC curves presented in both the Fig.s 7 (a) and (b) have sharply increased (negatively) and inversed MC responses at the bias voltages near the V_{oc} . However, the magnitude of MC response for P3HT:PCBM/Ca-device is relatively low ($< 0.1\%$) as compared to that of P3HT/Ca-device (Fig. 5) at the applied bias lower than the V_{oc} (~ 0.59 V for P3HT:PCBM/Ca-device). This observation can be interpreted in terms of quenching most of the photo-excited excitons and PP states (magnetic-sensitive) by the separation of oppositely charged carriers at the P3HT-PCBM (donor-acceptor) interface. Consequently, the P3HT:PCBM/Ca-device has the low MC responses at the bias voltages lower than the V_{oc} . Nevertheless, the observed MC responses at $V < V_{oc}$ are negative and increased negatively with the applied magnetic field. We suggest that the negative MC responses are due to the reduced charge reactions of excitons in P3HT-PCBM/Ca-device by the applied magnetic field, in which the excitons probably are generated by the back transfer of the charge-transfer complex states at the high magnetic field. However, this assumption needs more investigations in detail. The sharply increased (negatively) MC response at bias voltage of 0.59 V in Fig.s 7(a) and (b) is suggested to be due to the drastic reduction of the denominator $I(0)$ in Eq. (1), which is nearly zero at the bias voltage close to V_{oc} . The inset of Fig. 7(a) shows the MC curves at the enlarged scale as the biased voltages are nearby V_{oc} . Those curves have a threshold of MC response at the low

magnetic field and are increased negatively or positively at the high magnetic field, which are associated with the presence of intermolecular charge-transfer complexes in the donor-acceptor interface as discussed in the previous paragraph.

Summary

In summary, the mechanisms to interpret the MC responses for polymer photovoltaic devices made of P3HT and P3HT:PCBM as the active layers are presumably correlated with the influence of the applied magnetic field and electrical bias on the photo- and electrical-excited states (excitons and PP states) and intermolecular charge-transfer complexes of conjugated molecules. Our results have indicated that the MC responses can be modulated to yield positive, negative, and/or inverse effects by the photo illumination, the usage of different metal electrodes, interfacial dipole layer, the applied magnetic field and electrical bias, and the composition of polymer active layers. We regard the studies to change the excitation light intensity and wavelength would be essential to verify the origin of the device current (injected or photo-induced) in organic/polymer photovoltaic devices and further understand the mechanisms of MC responses. [64] This part of research is important and in progress at this time. As for P3HT:PCBM-based bulk-heterojunction photovoltaic cells, the charge-transfer complexes would be the critical excited states to influence the overall power conversion efficiency. The magnitude of photocurrent as well as the device performance can be further improved, if the dissociation of intermolecular charge-transfer complexes is facilitated, probably by manipulating and optimizing the bulk-heterojunction and the polymer/electrode interfaces. The studies to understand the intermolecular charge-transfer complex states in the active layer under the influence of applied magnetic field are currently underway.

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Figure Captions

FIG. 1. (a) The formation of intra- and inter-molecular excited PP states from excitons (b) The singlet and triplet electronic configurations of excitons and PP states (c) A schematic drawing for the processes of the positive, negative and net MC responses.

FIG. 2. (a) A schematic drawing that illustrates the device configuration, the measurement of MC responses for the polymer diodes under the applied magnetic field with illumination, and the chemical structures of P3HT and PCBM in this study. SMU represents the source measurement unit. (b) (●) The emission spectrum of halogen lamp and the absorption spectra of (■) P3HT and (◆) P3HT:PCBM films used in this studies.

FIG. 3. MC curves of the I_{sc} (photocurrent measured at 0V bias voltage) for P3HT/Al-device (○) and P3HT/Ca-device (□) with illumination by a halogen lamp (white light) at the intensity of 80 mW/cm².

FIG. 4. MC curves of the I_{sc} (photocurrent measured at 0V bias voltage) with illumination by a halogen lamp (white light) at the intensity of 80mW/cm² for P3HT/LiF(X nm)/Ca-device at B=1000mT of X= (□) 0, (△) 1.5, and (■) 5.0. The inset presents the thickness of LiF layer versus (○) MC response at B=1000mT and (●) I_{sc} plots.

FIG. 5. (a) MC curves of P3HT/Ca-device with illumination by a halogen lamp (white light) at the intensity of 80mW/cm² in the bias voltages of 0V (○), 0.50V (□), 0.90V (◇), 1.00V (△), 1.10V (▽), and 1.50V (●) (b). MC curve (□) of the P3HT/Ca-device with illumination versus bias voltage at B=1000mT and semi-logarithm current-voltage (J - V) plot (○).

FIG. 6. MC curves of P3HT/Ca-device (\circ) and P3HT:PCBM/Ca-device (\square) at the applied bias voltage, 2.00V and 0.70V, respectively, larger than its V_{oc} without illumination.

FIG. 7. (a) MC curves of P3HT:PCBM/Ca-device with the illumination by a halogen lamp (white light) at the intensity of 80 mW/cm² at bias voltages of 0.50V (\circ), 0.56V (\square), 0.58V (\diamond), 0.59V(\blacksquare), 0.60V (\triangle), 0.62V (∇) and 0.64V (\bullet). The inset shows the MC curves at enlarged scale at the biased voltages of 0.50V (\circ), 0.56V (\square), 0.58V (\diamond), 0.62V (∇) and 0.64V (\bullet). (b) MC curve (\square) of the P3HT:PCBM/Ca-device with illumination versus bias voltage at B=1000mT and semi-logarithm current-voltage (J - V) plot (\circ).

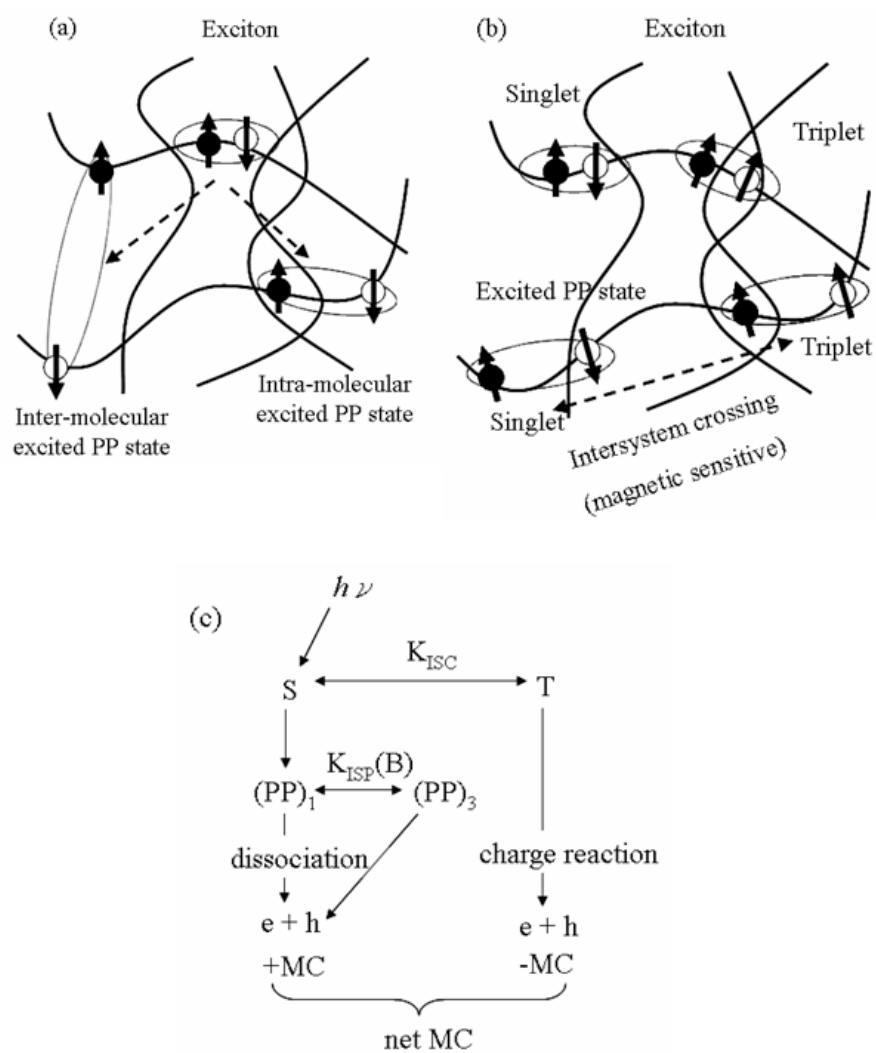


Figure 1.

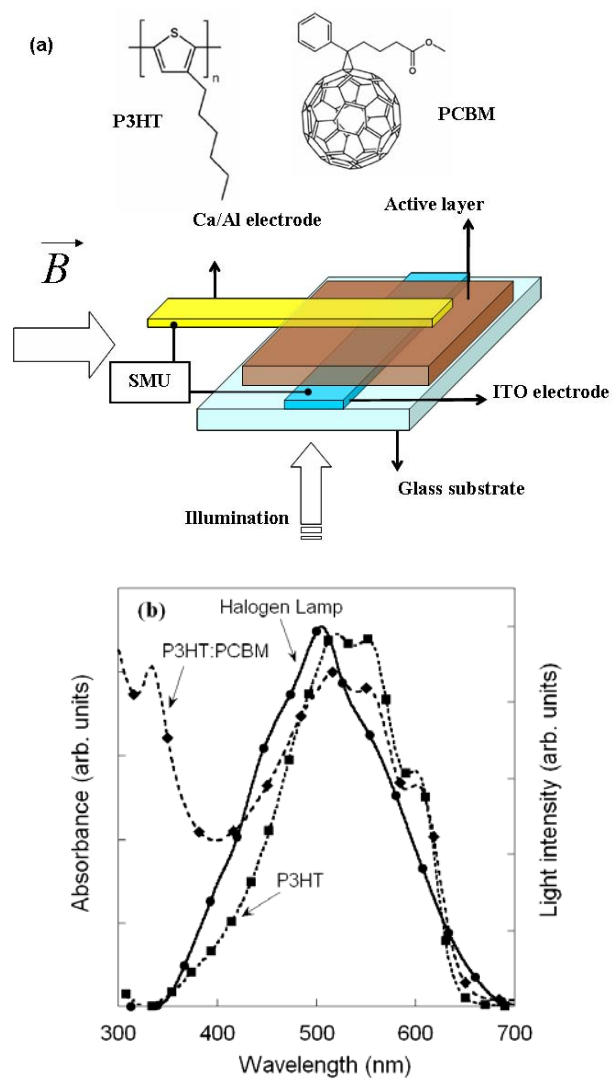


Figure 2.

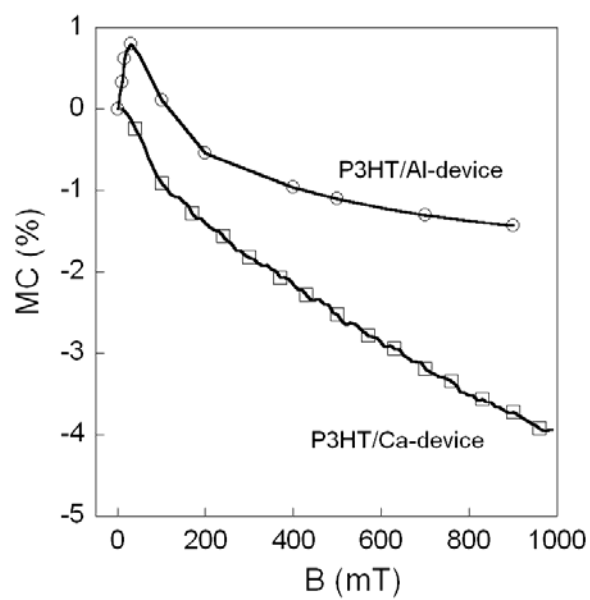


Figure 3.

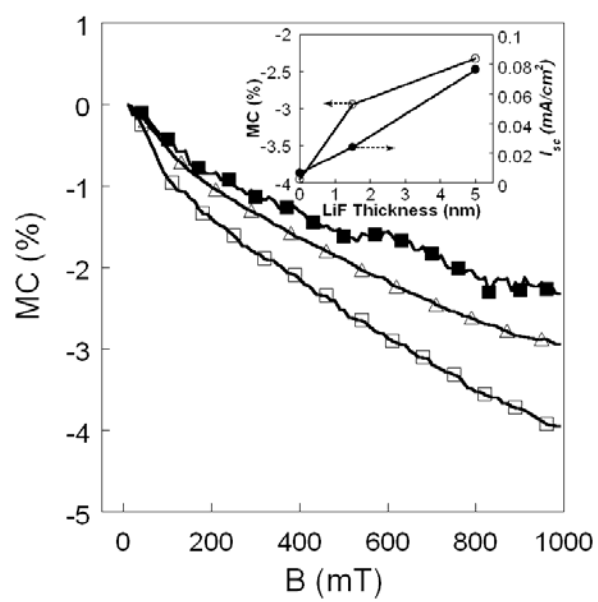


Figure 4.

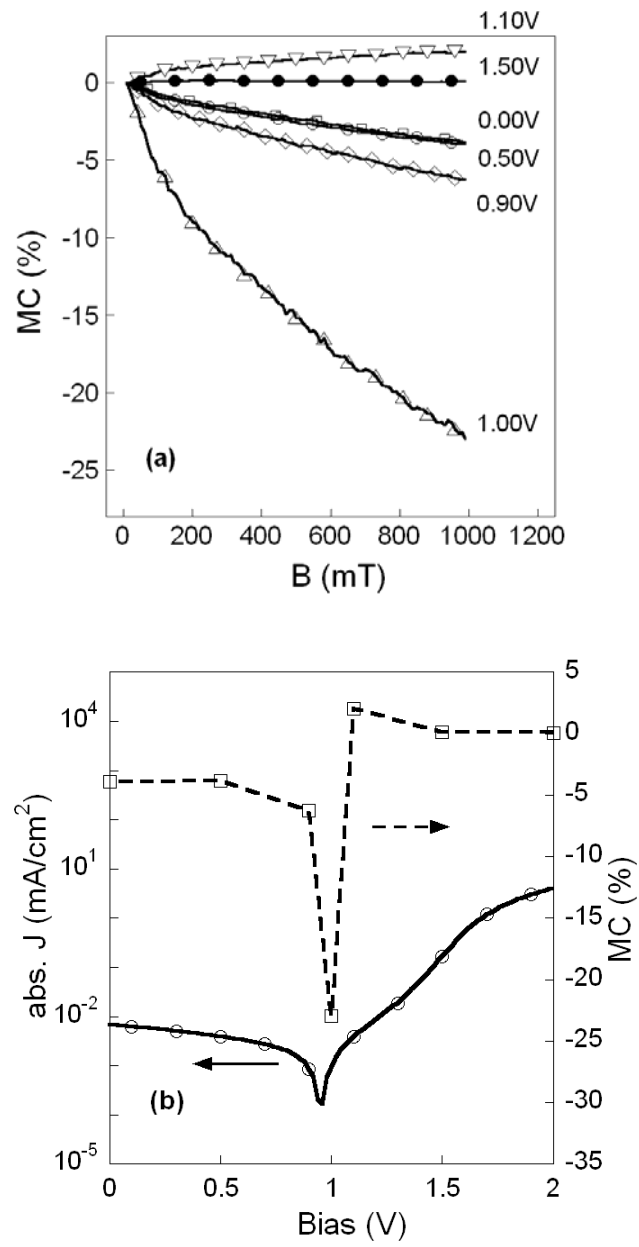


Figure 5.

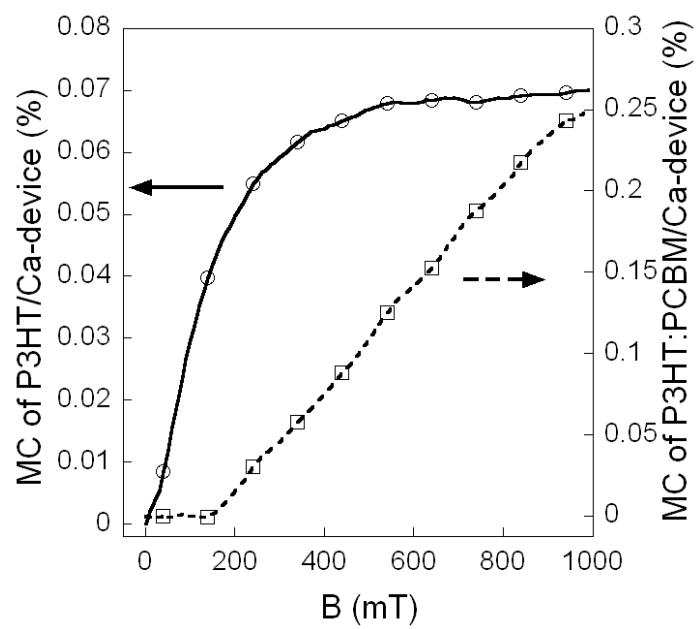


Figure 6.

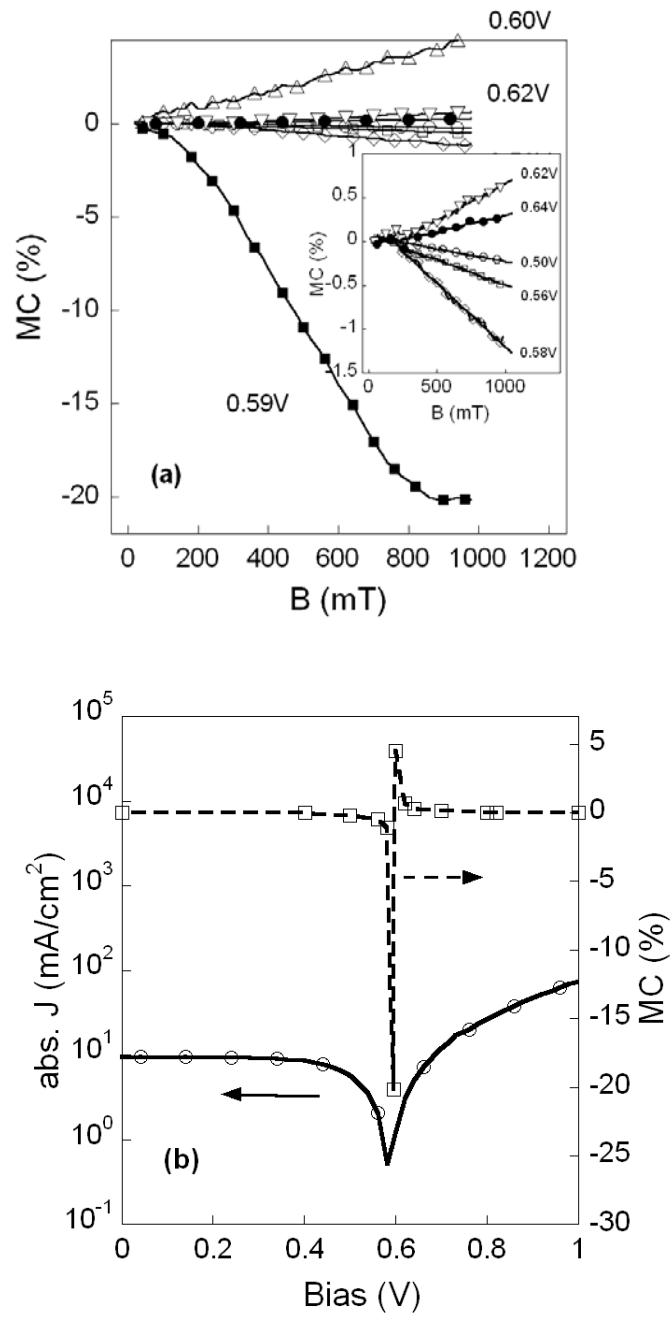
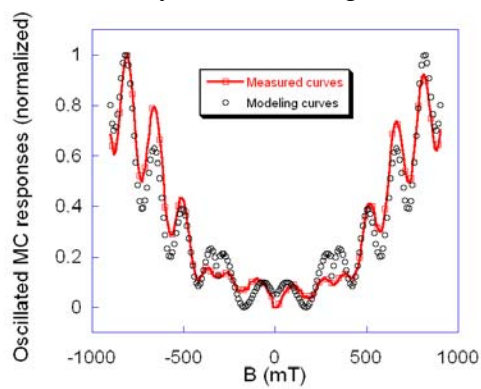


Figure 7.

V. Future work

- The P3HT:PCBM-based BHJ solar cells prepared by co-evaporating the poly(ethylene-oxide) functionalized polymer with Al metal as complex electrodes at different deposition ratio had shown the promising *PCE*. We will continue the XPS and UPS measurement at National Synchrotron Radiation Research Center, Taiwan to understand the working mechanism for the enhanced device performance. Our measurements suggested the work function of organic:metal complexes can be modulated by the ratio of co-evaporated poly(ethylene-oxide) functionalized polymer and Al. These also gave us a hint to manipulate the injection and transport of charge carriers by varying the compositions (ratios) of the interfacial organic:metal complex layer. Micro Raman, Fourier transform infrared spectroscopy, and Atomic force microscopy will also be used to characterize the unique interface at the polymer/metal junction. In addition, polymer photovoltaic cells made of different active layers will be used to evaluate the function of the organic:metal complex electrode.
- The modification of TiO₂/ITO substrate by self-assemble monolayer with different functionalities will be conducted to evaluate the improvement of the performance and the environmental stability of inverted-type organic/polymer light-emitting diodes and solar cells.
- The studies of magneto conductance (MC) responses of polymer photovoltaic cells is a joint research work with Prof. Bin Hu at University of Tennessee. We have the very promising results about the studies of MC responses for photovoltaic devices. Prof. Hu and we have a joint manuscript published in *Org. Electron.* **11**, 677 (2010). In addition, two other manuscripts about the studies of charge-transfer complex and the spin-injection, respectively, will be submitted soon. We will keep the close cooperation on the research projects together in future
- The studies of periodically oscillated magnetocurrent or magnetovoltage will be processed with the cooperation of Prof. Hu. We had confirmed that the periodically oscillated MC responses occur at devices made of the active layers containing the donor-acceptor conjugated molecules and operated at the effective bias voltage $\sim 0V$. The existence of charge-transfer complexes in conjugated molecules is critical to MC responses. The theoretical simulation of the periodically oscillated MC responses are proceeded as shown in the following figure. We would expect to be able to



demonstrate a prototype organic “magnetovoltaic” device in future.

VI. Conclusions

The poly(3-hexylthiophene) (P3HT):[6,6]-phenyl C61-butyric acid methyl ester (PCBM)-based bulk-heterojunction (*BHJ*) solar cells can be fabricated by applying the poly(ethylene oxide) functionalized Al electrodes, which are prepared by thermally evaporating (or co-evaporating) a thin layer of poly(ethylene glycol) dimethyl ether (PEGDE) (M_n ca. 2000) with Aluminum (Al) in vacuum (10^{-6} torr). The interfacial properties of Al electrode in *BHJ* solar cells were markedly improved by the unique organic/Al buffer structure. The instant formation of a carbide-like junction at the ethylene oxide/Al interface during the vacuum thermal evaporation, as characterized by the XPS and UPS analysis in National Synchrotron Radiation Research Center, Taiwan, is essentially important to the transport of electrons at Al electrode as well as the improved open-circuit voltage (V_{OC}) and power conversion efficiency (PCE) of devices. The V_{OC} and PCE of P3HT:PCBM-based solar cell fabricated with Al electrode without the post-annealing process of devices are 0.44V and 1.25%, respectively, and largely enhanced to 0.60 and 3.40% for the device applying PEGDE(4.5 nm)/Al(100nm) electrode. The P3HT:PCBM-based solar cells applying the co-evaporated PEGDE:Al buffer structures, such as PEGDE:Al(co-evaporation ratio of 1:1, 2:1, and 3:1, 5 nm)/Al(100nm), are also prepared, which has a maximum V_{OC} of 0.58V and PCE of ~ 4.0% for device made of PEGDE:Al(2:1, 5 nm)/Al functionalized electrode. The device performance can be modulated by the co-evaporating ratio of PEGDE:Al complex layer, due to the tunable work functions of the functionalized electrode as measured by UPS measurement.

We had measured the nano-scale mechanical properties of P3HT:PCBM blend films, prepared under different processing conditions and evaluated by nanoindentation. Photovoltaic devices fabricated using above active layers presented the highest power conversion efficiencies of blend films having lowest Young's modulus (20.73 GPa) and Hardness (649 MPa) at the optimized conditions of blend proportion (1:1), film drying-rate (slow), annealing temperature & time (110 °C & 10 min). It implies that the degree of nano-scale phase separation for the P3HT:PCBM blend is strongly correlated with the mechanical properties in the nano dimension. The nanoindentation is a method to estimate nano-scale mechanical properties of blend films and the performance of photovoltaic cells.

The dissociation and the charge-reaction processes of the photo-excited states in organic semiconductor layers that transform into free charge carriers are found to be changed by the applied magnetic field and essentially important to MC responses in

organic/polymer diodes and PV cells. The operation mechanisms (Magnetovoltaic effect) to extract the excited-state energy through the steady magnetic field are currently still in progress.